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Condensing agents in polycondensation

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ABSTRACT. The advances have been examined and trends noted in the development of a new method of synthesis of heterochain polymers which has been called "direct polycondensation" and is based on the interaction of monomers under mild conditions in the presence of various condensing agents. The latter form reactive derivatives with one of the monomers, which then react *in situ* with the monomer of the opposite nature. It has also been shown that the condensing agents can be used successfully in the synthesis of activated dicarboxylic acid diesters and diamides, which are promising electrophilic monomers for the synthesis of a wide variety of heterochain polymers under the conditions of low-temperature polycondensation in solution. The possibilities of the synthesis of polymers by the "biochemical" activation of monomers, i.e. using enzymes as "condensing agents", are discussed.

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I. Introduction

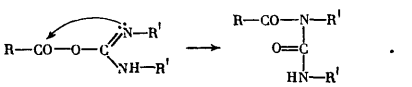
The polycondensation of dicarboxylic acids with diamines, diols, and other difunctional and polyfunctional nucleophiles proceeds as a rule only at high temperatures (up to 250–300 °C) and at a low rate and is accompanied by numerous side reactions leading to the decomposition of the functional groups and the breakdown of heterounit structures.[1] In a number of instances, for example, when aromatic diamines are used in polycondensation, high-molecular-weight polymers are not formed even at the high temperatures stated above.[2]

One of the most effective and widely used methods of overcoming the above difficulties consists in the employment of the corresponding acid halides (mainly dichlorides), which are distinguished by a high reactivity and which permit the synthesis of high-molecular-weight heterochain polymers at low temperatures (–30 to + 50 °C).[3–5] However, each individual acid dichloride must be synthesised and brought to the required condition, which involves additional expense. The high hydrolytic instability of acid dichlorides, which, apart from the destruction of the functional groups, leads to the evolution of hydrogen chloride, causes corrosion of the apparatus. The synthesis of acid dichlorides therefore requires additional complex apparatus made of corrosion-resistant materials.

In the light of the foregoing, the idea of employing a wide variety of reagents the so called condensing agents (CA), leading to the activation of one of the monomers (more precisely either electrophilic or nucleophilic functional groups) with their subsequent polycondensation *in situ* under mild conditions in organic solvents, is extremely attractive.

In synthetic organic chemistry, CA have been known for a fairly long time. A wide variety of halogen transferring agents ($SOCl_2$, PCl_3, $POCl_3$, etc.,[6] hexachlorocyclotriphosphazene,[7] cyanuric chloride,[8] picryl chloride,[9,10] picryl fluoride,[11] $SiCl_4$,[12–14] and $TiCl_4$[15]), carbonates,[16,17] sulphites,[18] carbodiimides,[19] a wide variety of phosphorus derivatives.[20–29] including derivatives immobilised on monomeric carriers,[30,31] polyphosphates,[32] as well as other compounds[33–35] have been used as highly effective CA. The employment of the above CA permits the successful solution of many complex synthetic problems, especially when water-soluble CA are used (see, for example, Woodward et al.[33] and Kemp and Chien[34]), which make it possible to form the amide bond or bonds of a similar nature in an aqueous medium. The employment of the above agents in peptide chemistry[12,14,18,20–22,25,26,33,34,36–40] and oligonucleotide chemistry[41] for the construction of peptide and phosphodiester bonds under mild conditions without the preliminary activation of the reactants has proved especially fruitful. This approach had hardly been used for polycondensation systems up to the beginning of the 1970's. A possible reason for this may be sought in the nature of the condensing agents commonly employed at the time in the peptide and nucleotide chemistry (dicyclohexylcarbodiimide, carbonyldiimidazole, etc.), which tended to undergo side reactions involving the destruction of the functional groups. This factor may not be so significant in the synthesis of individual low-molecular-weight substances (at worst it leads to a decrease in the yield) but is of primary importance in the synthesis of high-molecular-weight compounds, while the single-channel nature of the reaction (i.e. the absence of side processes involving chain termination) is a decisive factor for the attainment of high molecular weights.

The CA employed to construct the amide or ester bond form an activated intermediate with an electrophile (carboxylic acid, CO_2, or CS_2—see below) or a nucleophile; this then reacts further with a substrate of the opposite nature. The main requirement which must be met by such intermediate activated compounds is a sufficiently high stability (lifetime) and a low tendency to rearrange or undergo similar side reactions involving the destruction of the functional group. For example, the main disadvantage of carbodiimides as CA is the high tendency of the intermediate activated adduct to rearrange to an inactive acylurea:[19]



The introduction of various phosphorus compounds (both trivalent and pentavalent) as CA into the polymer chemistry made it possible to solve successfully the problem of the synthesis of high-molecular-weight polymers under the conditions of "direct polycondensation".

Subsequently other CA without phosphorus were also proposed. The prospects for the employment of various enzymes belonging to the class of hydrolases as CA are being discussed.

II. Phosphorus compounds as condensing agents

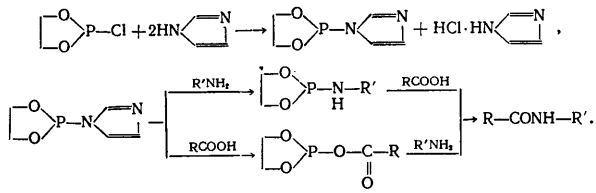
Phosphorus compounds, especially pyrophosphoric acid esters, were used as early as the 1950's–1960's in polycondensation (of the AB type) as CA for the synthesis of regularly alternating polypeptides. For example, polypeptides[20–22] with a molecular weight up to 25 000[22] were synthesised using tetraethyl pyrophosphate. However, up to the 1970's no systematic studies in the field of "direct polycondensation", involving also other "usual" monomers (among them those of the AA–BB type) were performed.

At the beginning of the 1970's, two groups of investigators (Ogata and co-workers and Yamazaki and Higashi) published almost simultaneously a series of communications on the successful use of phosphorus compounds as CA for the direct polycondensation of dicarboxylic acids with diamines and diols to form the corresponding polyamides and polyesters and initiated thereby systematic studies on a new promising field of synthesis of polymers.

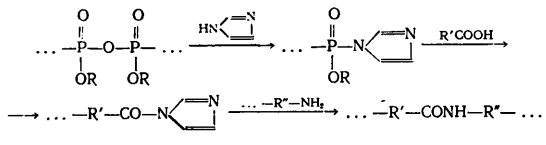
In their first publications, Ogata and co-workers[42,43] described the use of triphenyl phosphite $P(OPh)_3$ in the presence of imidazole as the CA and a somewhat modified version of the method proposed by Mitin and co-workers for the synthesis of peptides.[23] The authors suggest that the polycondensation proceeds with formation of an intermediate mixed anhydride, which reacts further with the diamine to form a polyamide:[43]

$$HOOC{-}R{-}COOH + 2P(OPh)_3 \xrightarrow{\text{imidazole}} (PhO)_2P{-}O{-}CO{-}R{-}CO{-}O{-}P(OPh)_2.$$

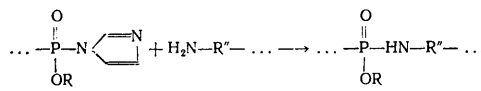
The mechanism and kinetics of the polycondensation reaction have been investigated in detail.[44] Apart from $P(OPh)_3$, its chloro-, methyl-, and methoxy-substituted analogues as well as 2-chloro-1,3,2-dioxaphosphorane (ethylene phosphorochlorodite) were used in the above reaction. The dioxaphosphorane reacts with imidazole to form 2-(1-imidazolyl)-1,3,2-dioxaphosphorane, which is capable, in its turn, of activating both an electrophile and a nucleophile:



In subsequent studies,[45] other phosphorus compounds were also used to synthesise polyamides, namely polyphosphoric acid esters (polyphosphates) in combination with imidazole. The mechanism of the activation put forward by the authors includes the formation of an acylimidazole, which has an exceptionally high acylating potential:

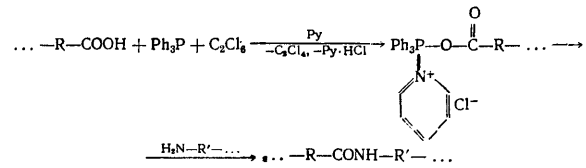


However, together with the reaction investigated, the formation of a relatively inactive phosphamide takes place at an appreciable rate, which is apparently in fact the main cause of the arrest of chain growth:



However, we cannot fully exclude chain termination due to the alkylation of amines, because it is known that phosphoric acid esters are fairly vigorous alkyl group transferring agents.[46]

The triphenylphosphine plus organic polyhalide condensing system[24,25] modified by pyridine[47–52] proved to be very successful. The proposed activation mechanism is as follows in this instance:



The above condensing system has been used to synthesise polyamides[46,48,52] and polyesters.[47,50]

Triphenylphosphine dichloride (plus a tertiary amine), which is in all probability actually an intermediate in the interaction of triphenyl phosphine with C_2Cl_6 when the reaction is carried out in accordance with the above scheme, has also been used successfully to synthesise polyesters.[53] A characteristic feature of this system is the possibility of regenerating the CA, which is important from the standpoint of the practical application of the method:

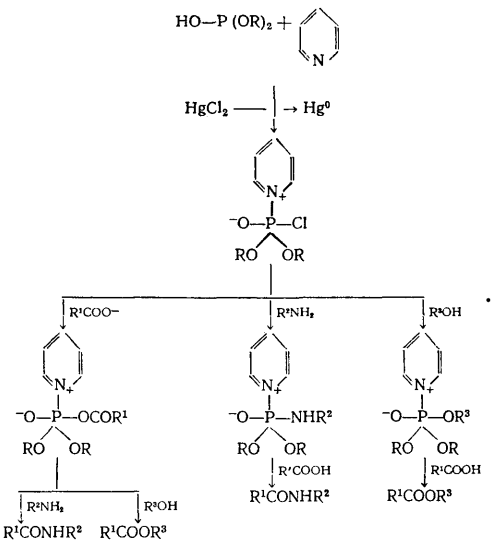
$$n\text{HOOCArCOOH} + n\text{HOAr'OH} \xrightarrow{2Ph_3PCl_2,\ B_N}$$
$$\longrightarrow -[-\text{COArCOOAr'O}-]_n- + Ph_3PO + B_N\cdot HCl,$$
$$Ph_3PO + COCl_2 \text{ (or ClCOCOCl)} \longrightarrow Ph_3PCl_2 + CO_2 + (CO);$$
$$B_N = \text{tertiary amine.}$$

High-molecular-weight polyesters based on bisphenol A and isophthalic acid (η_{int} = 2.24 dl g^{-1}) and *m*-hydroxybenzoic acid (η_{int} = 2.33 dl g^{-1}) have been obtained using phosphorus compounds, the best results being achieved in the presence of polymeric matrices—poly-2-vinyl- and poly-4-vinyl-pyridines or polyepoxyethane.[51]

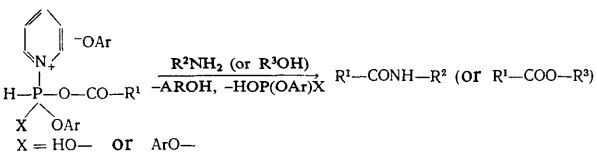
As regards the synthesis of polyamides, in the presence of the $P(OPh)_3$–imidazole system[42–44] low-molecular-weight polyamides with $\eta_{int} < 0.4$ dl g^{-1} were obtained from aliphatic monomers (salts of type AG). This is apparently due to the formation of appreciable amounts of comparatively inactive phenyl esters of carboxylic acids when imidazole is used as the tertiary amine in systems of this kind.[44] The polyphosphate–imidazole system also leads only to the synthesis of low-molecular-weight polyamides ($\eta_{int} < 0.3$ dl g^{-1}) for reasons discussed above.[45] The η_{int} for aliphatic polyamides was raised to 0.76 dl g^{-1} using the PPh_3–organic halide–pyridine system.[52] The system proved to be suitable for the synthesis of aromatic polyamides[47,49,50] especially of poly-*p*-benzamide, whose η_{int} was raised to 5.16 dl g^{-1}.[59] (For the halides employed, see Table 3 below.)

Since 1972, another group of investigators (Yamazaki, Higashi, and co-workers) also undertook systematic studies of a wide variety of phosphorus-containing condensing systems and of their employment both in the direct polycondensation and in peptide synthesis.[54–107] In their first publications, the authors established that the *N*-phosphonopyridinium derivative in the presence of an oxidant ($HgCl_2$) is

extremely reactive towards nucleophiles and activates carboxy- (interacting in the form of the carboxylate anion), amino-, and hydroxy-groups leading to the formation of the corresponding amides and esters on subsequent aminolysis, alcoholysis, or acidolysis:[54,56–58]

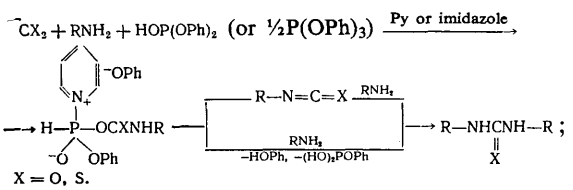


It was subsequently established that phosphates, in particular di- and tri-aryl phosphites, react with carboxylic acids, in the presence of pyridine but without an oxidant, to form the corresponding activated derivatives capable of further interaction with nucleophiles under mild conditions:[55]



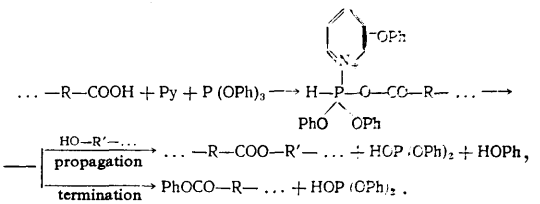
Apart from phosphites, other phosphorus compounds can also be used in similar reactions—phosphinites (R_2P-OAr), phosphonites [$R-P(OAr)_2$], phosphonates [$R-P(O)(OAr)_2$], etc., which are presented in Table 1. Only the aryl esters are effective.[65] We may note that the promoting role of pyridine and imidazole (and also of other bases having properties similar to theirs—Table 2) is in all cases significant. Promoting functions are also performed by *N*-methylpyrrolidinone (*N*-MD) (which is in addition the most suitable solvent in the processes indicated) and tetramethylurea. Various organic halides (Table 3) as well as metal salts, particularly LiCl and $CaCl_2$ (Table 4), quaternary ammonium salts, and tertiary amine hydrochlorides (Table 5) are also effective promoting agents in the reactions of aryl phosphites described above.

The main advantages of the systems examined include the fact that the reaction is performed in one stage by adding the CA directly to the mixture of the electrophile and the nucleophile. It is essential to note that, apart from carboxylic acids, in the presence of pyridine or imidazole aryl phosphites form activated derivatives with CO_2 (or CS_2), which leads to the "direct" synthesis of the corresponding ureas:[64]

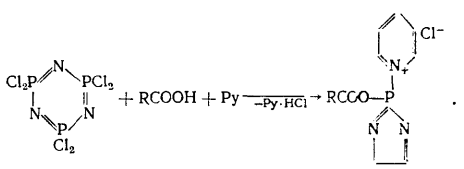


Various halogen-containing phosphorus compounds, namely $PhOPCl_2$,[69,70] $EtOPCl_2$, $PhPCl_2$, $(PhO)_2PCl$, $(EtO)_2PCl$, etc.,[70] have likewise been used as CA in order to synthesise ureas from CO_2. In the synthesis of polyureas, for example, from di(4-aminophenyl)-methane (t = 40 °C, P_{CO_2} = 20 atm), the systems $P(OPh)_3$ + imidazole in dimethylformamide (η_{ln} = 0.37 dl g^{-1}) and $HOP(OPh)_2$ in pyridine (η_{ln} = 2.24 dl g^{-1}) proved to be the most effective. The $PhOPCl_2$ system in pyridine made it possible to synthesise polyureas at atmospheric CO_2 pressure (η_{ln} = 0.4–0.5 dl g^{-1}).[69]

Aryl phosphites, which are excellent CA in the processes indicated above (in the synthesis of polyamides or their analogues), proved to be relatively ineffective in the synthesis of polyesters, which has been attributed to chain termination as a result of the competing intramolecular esterification reaction:[83]



The best CA in the synthesis of polyesters are pentavalent phosphorus compounds containing a phosphorus–chlorine bond. Thus polyesters (η_{ln} = 0.2–0.8 dl g^{-1}) have been synthesised successfully in the presence of hexachlorocyclotriphosphazene.[75,85,89] It is believed that the reaction proceeds via *N*-phosphinopyridinium derivatives:



Polyesters with higher molecular weights have been obtained by employing the $(PhO)_2P(O)Cl-LiCl$ system in pyridine,[98,101,103] best results being achieved in the presence of *NN*-disubstituted amides (forming Vilsmeier adducts with the CA),[101,103] especially dimethylformamide. The same system has been used successfully to synthesise

Table 1. The phosphorus compounds used as CA.

No.	Phosphorus compound	Effect*	Refs.
	Phosphorus (III) compounds		
1	$P(OH)_3$	–	[66]
2	$HO-P(-OC_2H_5)_2$	–	[66]
3	$HO-P(-OC_4H_9)_2$	–	[66]
4	$HO-P(-OCH_3)(-O\overset{+}{N}H_4)$	–	[66]
5	$HO-P(-OC_2H_5)_3+I_2$	++	[139]
6	$HO-P(-O-C_6H_5)_2$	++	[55, 59–61, 63, 64, 66–68, 71–73, 78, 84, 92, 119, 121]
7	$P(-OC_2H_5)_3$	–	[43, 66, 67]
8	$P(-OC_4H_9)_3$	–	[66]
9	$(C_2H_5O-)_2P-O-C(CH_3)=CH-CO-CH_3$	++	[94]
10	$P(-O-C_6H_5)_3$	++	[42–44, 62, 63, 66, 67, 71–80, 82, 83, 87, 92, 95, 96, 99, 100, 109–119, 121–123, 127, 133, 134, 140–148, 153, 155–158]

Table 1 (contd.)

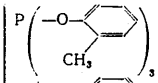
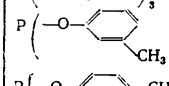
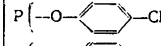
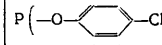
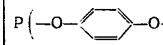
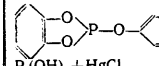
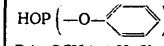
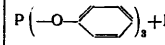
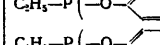
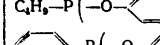
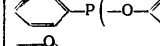
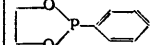
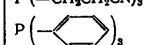
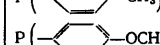
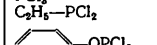
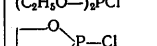
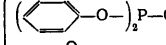
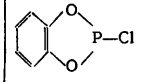
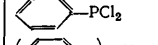
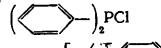
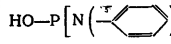
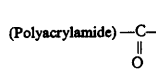
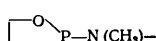
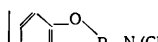
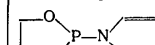
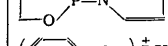
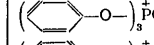
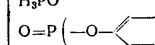
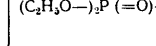
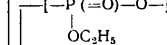
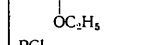
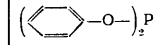
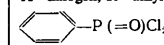
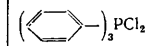
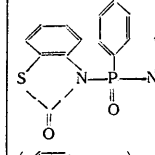
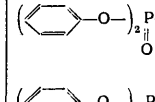
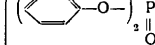
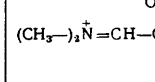
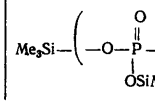
No.	Phosphorus compound	Effect*	Refs.
	Phosphorus (III) compounds		
11		++	[44, 62, 66, 67, 77, 119, 121, 122]
12		++	[44, 62, 66, 67, 72, 119, 121, 122]
13		++	[44, 62, 66, 67, 72, 119, 121, 122]
14		++	[44, 62, 66, 67, 119, 121, 122]
15		++	[44]
16		++	[43]
17	$P(OH)_3+HgCl_2$	++	[57]
18	$(HO)_2POC_2H_5+HgCl_2$	++	[57]
19	HOP $(-OCH_3)_3+HgCl_2$	+	[56]
20	HOP $(-OC_2H_5)_2+HgCl_2$	++	[56]
21	HOP $(-O-uзo\text{-}C_3H_7)_2+HgCl_2$	++	[56]
22	HOP $(-OC_4H_9)_2+HgCl_2$	++	[56]
23		++	[56, 59, 92]
24	$P(-OCH_3)_3+HgCl_2$	—	[56]
25	$P(-OC_2H_5)_3+HgCl_2$	+	[56]
26	$P(-O\text{-iso-}C_3H_7)_3+HgCl_2$	++	[56]
27	$P(-OC_4H_9)_3+HgCl_2$	+	[56, 66]
28		++	[56, 92]
29		++	[67, 72, 92, 122]
30		++	[122]
31		++	[122]
32		—	[43]
33	$P(-CH_2CH_2CN)_3$	++	[52]
34		++	[47—51, 86, 130, 151, 152]
35		+	[52]
36		+	[52]
37	PCl_3	++	[70, 127]
38	$C_2H_5—PCl_2$	++	[70]
39		++	[69, 70, 128, 129]
40	$(C_2H_5O—)_2PCl$	+	[70]
41		++	[44, 131, 132]
42		+	[70]
43		+	[70, 83]
44	R_xPCl_{3-x}, R = alkyl or aryl, $x = 1-3$	++	[70, 83, 119, 130]
45		++	[70, 83, 119, 130]
46		++	[83, 119]
47		++	[122]
48	$(C_2H_5O—)_2P—N(R')—COR$, R′ = H—, CH_3—	++	[102, 104]
49	$(C_2H_5O—)_2P—N=C(CH_3)—O—P(—OC_2H_5)_2$	++	[104]
50		++	[104]
51		++	[102]

Table 1 (contd.)

No.	Phosphorus compound	Effect*	Refs.
	Phosphorus (III) compounds		
52	 R = H, CH_3, OC_2H_5, CF_3, $(C_2H_5O)_2P$	++	[102]
53		++	[44]
54		++	[74]
55		++	[74]
	Phosphorus (V) compounds		
56	P_2O_5	++	[135]
57	H_3PO	—	[43]
58		—	[43]
59	$(C_2H_5O—)_2P(=O)—O—P(=O)(—OC_2H_5)_2$	++	[20—22, 45, 81]
60	$(C_2H_5O—)_2P(=O)—(O—P(=O)—)_n—$  $—P(=O)(—OC_2H_5)_2$ $n=1,2$	++	[45, 81]
61		++	[45]
62		++	[81]
63	PCl_5	—	[70]
64	$O=PCl_3$	—	[70]
65		++	[97, 98, 101, 103, 105—107, 120, 124, 125]
66	$(RO—)_2P(=O)—X$ X = halogen, R = alkyl or aryl	++	[120]
67		—	[70]
68	$(—N=PCl_2—)_3$	++	[75, 85, 89, 92, 119, 123]
69		+	[53]
70	$P_2O_5+CH_3SO_3H$		[160, 161]
71		++	[137]
72		++	[138]
73		++	[154]
74		++	[206]
75		++	[159]

Remarks. (++)—the product is formed in a yield > 50%; (+)—the product is formed in a yield ⩽ 50%; (—)—the product is formed in a yield < 10—15% or is not formed at all.

*The table indicates the tendency of the CA towards the formation of a product in a particular yield because in many instances they were tested only in model reactions; compounds forming a product in a yield exceeding 50% are as a rule effective in polycondensation.

Table 2. The bases tested in direct polycondensation by the phosphorylation method.*

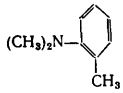
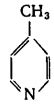
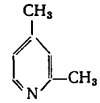
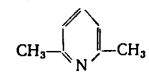
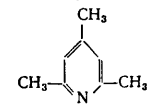
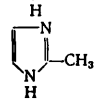
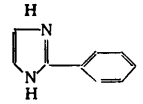
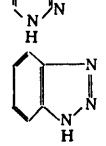
Base	Effect	Refs.
$(C_2H_5)_3N$	−	[43—45, 49, 51, 63, 66, 70, 119, 120, 137]
	−	[44]
	−	[49]
	+	[43, 44, 49—51, 59—77, 83, 84, 87, 90—92, 95—101, 103, 105—107, 109—120, 122—134, 139, 141—150, 153, 156—158]
	+	[49, 51, 52, 63, 66, 67, 70, 76, 99, 119, 122]
	+	[49, 51, 52, 63, 66, 67, 70, 76, 99, 119, 122]
	+	[44, 49, 51, 52, 63, 66, 67, 70, 76, 99, 119, 122]
	+	[49, 99]
	+	[67, 70, 122]
	+	[44, 49, 63, 66, 67, 70, 76, 122]
	+	[99]
	+	[49, 51, 155]
	+	[120]
	+	[42—45, 55, 63, 66, 67, 81, 86, 94, 99, 119, 139]
	+	[44, 45, 120]
	+	[44]
	+	[120]
	+	[44, 45]
	+	[45]
	+	[44, 45]

Table 2 (contd.)

Base	Effect	Refs.
$(CH_3)_2N—CO—N(CH_3)_2$	+	[49]
N-Methylpyrrolidinone	+	[49]
Hexamethylphosphoramide	−	[49]
KOH	−	[43]

*Trivalent phosphorus compounds—di- and tri-aryl phosphites and triphenylphosphine—were used as the CA.

Table 3. The organic halides tested as promoting additives in direct polycondensation by the phosphorylation method.

Halide	Effect	Refs.
CH_3I	+	[74] *
C_6H_5Br	+	[74] *
CCl_4	+	[47, 51, 52, 86]
CBr_4	+	[47, 51, 52]
CI_4	+	[52]
$CHBr_3$	+	[52]
$Cl_3C—CCl_3$	+	[47—52]
$Cl_3C—CO—CCl_3$	+	[47, 51, 52]
$Cl_3C—CO—O—C_6H_4—O—CO—CCl_3$	+	[47, 51]
$Cl_3C—CO—O—uso\text{-}C_3H_7$	+	[
$Cl_2CH—CO—O—uso\text{-}C_3H_7$	−	:7]
$ClCH_2—CO—O—uso\text{-}C_3H_7$	−	7]
$Br_3C—SO_2—Ph$	+	[47]

*$(PhO)_3P$ was used as the CA by Yamazaki et al.,[74] while in the remaining cases Ph_3P was employed.

Table 4. The metal salts and complexes tested as promoting additives in direct polycondensation by the phosphorylation method.*

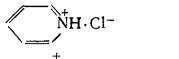
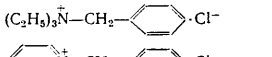
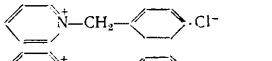
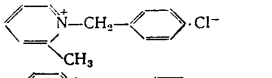
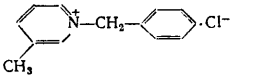
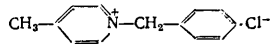
Additive	Effect	Refs.
LiCl	++	[67, 68, 72, 76—80, 82, 87, 92, 95—98, 103—106, 109, 113, 122, 127, 133—135, 140—150, 153, 156—158]
LiBr	+	[79, 105, 119, 120, 122]
LiF	−	[79]
$LiNO_3$	−	[79]
KBr	+	[79]
KI	+	[151]
KSCN	−	[67, 68, 72, 79, 92]
$CaCl_2$	++	[67, 68, 72, 79, 87, 92, 95, 96, 116—122, 135]
$CaCl_2·H_2O$	+	[67, 68, 72, 92]
$CaBr_2$	+	[121, 122]
$MgCl_2$	+	[44, 67, 68, 72, 79, 92, 119, 120, 135]
$NiCl_2$	−	[79]
$ZnCl_2$	+	[67, 68, 72, 79, 92]
$CuCl_2$	+	[44]
$Cu(OCOCH_3)_2$	+	[44]
LiAcAc	−	[67, 68, 72]
$Cu(AcAc)_2$	+	[44]
$Ni(AcAc)_2$	+	[44]
$Mg(AcAc)_2$	+	[44]
$Co(AcAc)_2$	+	[44]
$Zr(AcAc)_4$	+	[44]
$Fe(AcAc)_2$	−	[44]

Remarks. ++—strong effect, +—weak effect, −—no effect; AcAc = acetylacetonate; when introduced in small amounts (up to 4 mol%), acetylacetonates exhibit a catalytic effect; greater amounts (up to 100%) inhibit the reaction.

**Mainly trivalent phosphorus compounds—di- and tri-arylphosphites— were used as the CA.

various polyamidoesters (η_{ln} up to 1.93 dl g^{-1}).[103] It has the advantage, apart from those already mentioned, that the CA (diphenyl phosphorochloridate) can be regenerated by treating the diphenyl phosphate formed with thionyl chloride.

Table 5. The salts of tertiary amines used as promoting additives in direct polycondensation by the phosphorylation method in the presence of $(PhO)_3P$.

Salt	Effect	Refs.
$(C_2H_5)_3\overset{+}{N}H\cdot Cl^-$	++	[88, 99]
	++	[88, 99]
$(CH_3)_4\overset{+}{N}\cdot Cl^-$	+	[88]
$(C_2H_5)_4\overset{+}{N}\cdot Cl^-$	++	[88]
$(C_2H_5)_4\overset{+}{N}Br^-$	+	[88]
$(C_2H_5)_4\overset{+}{N}\cdot I^-$	+	[88]
$(C_4H_9)_4\overset{+}{N}\cdot Cl^-$	+	[88]
	++	[88]
	++	[88]
	++	[88]
	++	[88]
	++	[88]

Remarks. ++—strong effect; +—weak effect.

Yamazaki and co-workers[104] used a polymeric derivative of *N*-acylphosphoramidite (compound No. 50 in Table 1) as the CA for the synthesis of dipeptides. The use of similar compounds in polycondensation would be of interest, since this would greatly facilitate the removal of polycondensation side products from the reaction mixture and also the regeneration of the CA.

Using the above CA as well as a number of others, Yamazaki, Higashi, and co-workers achieved the syntheses of various high-molecular-weight film- and fibre-forming heterochain polymers: AA–BB and AB polyamides,[59,67,68,72,76–79,82,84,87,88,90–92,94,97,99,100,102,103,106] polyhydrazides,[78,84] polyaminoacids (α and β) and regularly alternating polypeptides,[55,60,62,63,71,80,92] AA–BB and AB polyesters,[75,81,83,86,89,92,97,98,100,101,103,105–107] and polyureas and polythioureas.[61,66,68,69,73,92,93] (Many CA proved to be effective also in the synthesis of peptides.[54,55,63,65,104]) The influence of various factors—the structure of the monomers, temperature, and the nature of the CA, promoting agents, and solvents—on the yield and the molecular weight characteristics of the target products has been investigated. These aspects of the process have been described in detail in the literature.[92,108] Here we shall mention only that high-molecular-weight polyamides can be obtained from aromatic diamines by the proposed direct polycondensation methods. Aliphatic diamines lead to the synthesis of low-molecular-weight polymers, which are relatively unpromising from the practical point of view. This has been attributed to the side interaction of the above diamines with the phosphorus compounds employed.

Subsequent communications by other investigators were devoted both to the solution of specific problems involving the application of condensing systems enumerated above and to the search for a series of new phosphorus-containing CA suitable for polycondensation designed to synthesise heterochain polymers of different classes.

Preston and co-workers[109–118] synthesised polyamides and polyhydrazides using the $P(OPh)_3-Py-LiCl$ system, having extended the Yamazaki–Higashi reaction to various aromatic diamines, dicarboxylic acids, and their hydrazides. It is of interest to note that they succeeded in synthesising poly-*p*-phenyleneterephthalamide with $\eta_{ln} = 6.2$ dl g^{-1} by means of direct polycondensation.

Azuma and co-workers[119–126] synthesised aromatic polyesters[119,120,124–126] and polyamides[121–123] using various diaryl phosphites, triaryl phosphites, chlorophosphines, hexachlorocyclotriphosphazene, chlorodiphenyl phosphate, etc.

A simplified method of synthesis of polyamides, where $P(OPh)_2$ was obtained from phenol and PCl_3 in solution in pyridine, has been described.[127] Without isolating $P(OPh)_3$, the reaction solution was used subsequently as the CA in the polycondensation of aromatic diamines with aromatic dicarboxylic acids. Polyamides with $\eta_{ln} \simeq 1.0$ dl g^{-1} were obtained.

Phosphorus compounds have been used to synthesise heterochain polymers by direct polycondensation,[130–132] including polyureas and polythioureas.[131,132] In the synthesis of the latter, ethylene phosphorochloridite was used as the CA.

Multiblock copolymers containing arylamide and polyoxyethylene fragments have been obtained in the presence of the $P(OPh)_3-Py-LiCl/CaCl_2$ system.[133]

The method of direct polycondensation in *N*-MP [the $P(OPh)_3-Py-LiCl$ system] has been used[134] to synthesise polyamides from *NN'*-terephthaloylbis-β-alanine (a diamidodicarboxylic acid whose dichloride is not obtainable) and hexamethylene diamine. However, despite the use of a wide variety of polymeric matrices [poly(ethylene oxide), poly-*N*-vinylpyrrolidinone, poly-4-vinylpyridine], only a low-molecular-weight polymer with $[\eta] = 0.14$ dl g^{-1} was obtained, which is typical for an aliphatic diamine.

P_2O_5 has been used as the CA for the synthesis of polyamides from aromatic diamines and dicarboxylic acids (both aromatic and aliphatic).[135] The reaction was performed in *N*-MP in two stages—initially a mixed anhydride of dicarboxylic acid and P_2O_5 was obtained (80 °C, 1 h), then the diamine was introduced into the solution and the polycondensation was carried out at 20 °C. Polyamides with $\eta_{int} = 0.18-0.85$ dl g^{-1} were obtained. However, it is essential to note that phosphorus pentoxide dehydrates aliphatic amides with formation of keten imines,[136] which can give rise to complications when aliphatic dicarboxyic acids are used. *NN*-Phenylene phosphonobis[2(3*H*)-benzothiazolone][137] and 1,2-benzoisoxazol-3-yl diphenyl phosphate[138] (Nos. 71 and 72 in Table 1) have also been used to synthesise polyamides.

A method of synthesis of various poly-α-aminoacids with a degree of polycondensation of approximately 50 using the $HOP(OC_2H_5)_2/I_2$ system in the presence of pyridine or imidazole as the CA has been described.[139]

The synthesis of polyamides, polyamidoimides, and polyamidohydrazides using the $P(OPh)_3-Py-LiCl$ system has also been described.[140–143] We may note that polyamides, distinguished by a satisfactory thermal stability, have been synthesised from cyclic aliphatic dicarboxylic acids.

Aharoni and co-workers[144–146] investigated thoroughly the mechanism of the polycondensation reaction with participation of phosphites and concluded that the formation of the *N*-phosphinopyridinium salt or of a mixed anhydride of the carboxylic and phosphorous acids, postulated in the studies examined above, does not occur. The diametrically opposite reaction mechanism, involving the formation of an intermediate aminodiphenoxyphosphine, was proposed:

$$P(OPh)_3 + H_2N{-}R{-}\ldots \xrightarrow[-PhOH]{} (PhO)_2P{-}NH{-}R{-}\ldots \xrightarrow{HOOC{-}R'{-}\ldots} \longrightarrow \ldots {-}R'{-}CONH{-}R{-}\ldots$$

In other words, according to the above workers,[144–146] the nucleophile and not the electrophile is activated, as would follow from the mechanism proposed by Yamazaki and Higashi. Their experimental data[144–146] are fairly convincing, but the role of pyridine solely as a promoting agent is not altogether clear. If pyridine functions only as a proton transferring agent, as suggested by the authors, then the same role could be played more successfully by other bases for example by hexamethylphosphoramide, which, however, is ineffective in the processes indicated (Table 2).

The polyamide extrusion process at 280–300 °C in the presence of small amounts (0.5–1.0%) of $P(OPh)_3$, accompanied by a sharp increase in the molecular weight of the polymer, proposed by Aharoni et al.,[145] is noteworthy.

Korshak and co-workers were the first to use the phosphorylation reaction in order to obtain high-molecular-weight polyamidophenylquinoxalines[147] and silicon-containing aromatic polyamides.[148] Polyamides with quinoxaline units have been synthesised by direct polycondensation using $P(OPh)_3$.[149,150]

A number of other studies have also been published in which a wide variety of heterochain polymers have been synthesised using phosphorus compounds as the CA: PPh_3 for the synthesis of polyesters,[151] PPh_3,[152] and $P(OPh)_3$[153] for the synthesis of polyamidoimides, and $(PhO)_2P(O)-N_3$[154] and $P(OPh)_3$[155–158] for the synthesis of regularly alternating polydipeptides and poly-α-aminoacids.

An interesting reaction involving the synthesis of polyamidines by the reaction of aromatic diamines with benzoic acids using poly(trimethylsilyl phosphate) as the CA, has been described.[159] An amide is formed in the first stage, reacting subsequently with the free aminogroup to form the amidine bond:

$$\ldots {-}Ar{-}NH_2 + HOOCAr' \xrightarrow[-H_2O]{} \ldots {-}Ar{-}NHCO{-}Ar'{-}\ldots \xrightarrow[-H_2O]{H_2N{-}Ar{-}\ldots} \ldots {-}Ar{-}NH{-}\underset{\displaystyle Ar'}{\underset{|}{C}}{=}N{-}Ar{-}\ldots$$

The $P_2O_5-CH_3SO_3H$ mixture has also been used in recent years as the CA in the reaction medium.[160,161] This system is particularly effective in the synthesis of polybenzazoles.

Thus it follows from the foregoing that the direct polycondensation reaction using phosphorus compounds has developed vigorously during the last 10–15 years. The phosphorus compounds proposed as the CA are listed in Table 1. Analysis of the available data shows that, bearing in mind their availability and the results achieved, diphenyl and triphenyl phosphites are the most common and promising substances among trivalent phosphorus compounds, while among pentavalent phosphorus compounds the most promising substance is diphenyl phosphorochloridate, which has the advantage that it can be regenerated after the reaction (see above).

When phosphorus compounds are used as the CA, promoting agents play a significant role, as already mentioned above (Tables 2–5). The exceptionally marked effect of a wide variety of polymers (Table 6), capable of forming hydrogen bonds with the monomers, must be especially emphasised. It was shown for the first time in a number of studies[51,76,77,80] that the introduction of polymers of the above type into the reaction solution increases significantly the rate of polycondensation and the molecular weight of the target polymers. The matrix effects of the added polymers consist in increasing the local concentration of the reactants and possibly in the attainment of their mutually convenient orientation in space. These considerations may be supported, for example, by the formation of high-molecular-weight polyaminoacids directly from free α-aminoacids (Val, Leu, Phe, Met) under direct polycondensation conditions $P(OPh)_3$ + LiCl] using poly-*N*-vinylpyrrolidinone (PDP) with molecular weights of 10^4, 4×10^4, and 3.6×10^5 as the matrix.[80] It has been established that the molecular weight of the final polyaminoacid increases with increasing molecular weight of the PDP and amounts to approximately 0.1 of the latter. In all probability, the matrix influences not only the molecular weight of the polyaminoacid synthesised but also the course of the reaction, directing it towards the formation of a linear polymer. The synthesis of poly-β-alanine from the free aminoacid has also been achieved under similar conditions.[80]

Table 6. The polymers tested as matrices in direct polycondensation by the phosphorylation method.

Polymer-matrix	Polymers synthesised	Phosphorus-containing agent	Effect*	Refs.
Poly(ethylene oxide)	Polyamides	$P(OPh)_3$, $HOP(OPh)_2$	+	[77, 82, 92, 121, 123, 134]
"	Polyesters	PPh_3, $(PhO)_2P(O)Cl$	+	[51, 107]
"	Polyα-amino-acids	$P(OPh)_3$	+	[156, 157]
Poly(ethylene oxide)-poly(propylene oxide) block copolymer	Polyamides	$P(OPh)_3$, $HOP(OPh)_2$	+	[121]
Poly-*N*-vinyl-pyrrolidinone	Polyamides	$P(OPh)_3$, $HOP(OPh)_2$	+	[82, 92, 121, 134]
"	Polyesters	$(PhO)_2P(O)Cl$	+	[107]
"	Polyaminoacids (α and β)	$P(OPh)_3$	+	[80]
Poly-2-vinyl-pyridine	Polyesters	PPh_3	+	[51]
Poly-4-vinyl-pyridine	Polyamides	$P(OPh)_3$	+	[76, 82, 92, 123, 134]
"	Polyesters	PPh_3, $(PhO)_2P(O)Cl$	+	[51, 107]
"	Poly-α-amino-acids	$HOP(OC_6H_5)_2+I_2$	+	[139]
Poly-*N*-*p*-tolyl-maleimide	Poly-α-amino-acids	$P(OPh)_3$	+	[158]
Polystyrene	Polyesters	PPh_3	—	[51]

*Increases the rate of reaction or the molecular weight of the polymer synthesised.

It is essential to note that, in contrast to matrix polymerisation, the characteristic features of which have been thoroughly investigated,[162] matrix polycondensation is a new and little investigated field. The reasons for this should apparently be sought in the inapplicability of the traditional low-temperature polycondensation methods in matrix synthesis, mainly owing to the unduly high reactivity of the monomers employed (acid dichlorides, bischloroformates, diisocyanates, etc.), capable of interacting irreversibly with the polymers used as the

matrices. The development in recent years of "high order" polycondensation methods leads to interesting prospects for the investigation of the matrix polycondensation in which there are, from our point of view, considerable possibilities for polymer chemistry.

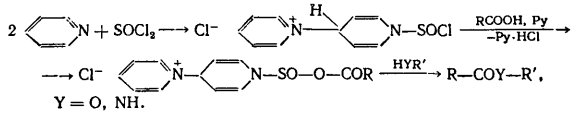
III. Phosphorus-free condensing agents

One of the first CA used successfully as early as the end of the 1950's[163,164] for the synthesis of polyhydroxyacids under the conditions of high-temperature polycondensation was thionyl chloride. The first communications about the applicability of $SOCl_2$ as the CA under the conditions of low-temperature polycondensation in the synthesis of polyamides were published by Ueda et al.[165] in 1978. Subsequently a series of studies devoted to this problem were published.[159,166–172] Regardless of the reaction conditions and the nature of the solvents and acceptors employed (tertiary amines) and also the method used to introduce the reactants, polyamides with $\eta_{int} \leqslant 0.6$ dl g^{-1} were obtained in the majority of cases.

A study devoted to the synthesis of polyesters (together with polyamides) under the conditions of low-temperature polycondensation using $SOCl_2$ as the CA was published in 1980.[166] Subsequently the synthesis of polyesters by the above method was achieved also by Maiti and co-workers,[170] who used dicarboxylic acid salts instead of the free acids themselves and also by Elias and co-workers.[173–175] Only low-molecular weight polyesters were obtained in most cases. Best results have been published by Elias and Warner,[173] who synthesised a polyester with $[\eta] = 0.96$ dl g^{-1} from 3-(*p*-hydroxyphenyl)propionic acid.

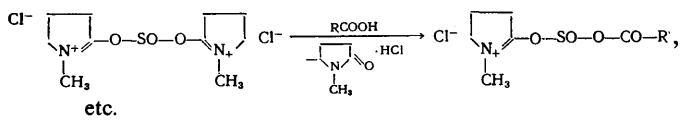
In the studies quoted, the polycondensation in the presence of $SOCl_2$ was carried out predominantly in two stages: the dicarboxylic acid was treated initially with a stoichiometric amount of $SOCl_2$ and then a nucleophile and a hydrogen chloride acceptor were added to the resulting solution. When the reactants are added in this order, the reaction proceeds via intermediate acid dichlorides and is apparently accompanied to a large extent by the side processes characteristic of the latter,[2–4] which is in fact the reason for the low molecular weights of the final polymers.

It has been established[176] that polyesters with much higher molecular weights (with η_{ln} up to 5.56 dl g^{-1}) are obtained when the mixture of dicarboxylic acid and the bisphenol (or an aromatic hydroxyacid) is treated with the complex $SOCl_2$.Py prepared beforehand at a low temperature. The authors suggest that the complex is converted on treatment with the carboxylic acid into the corresponding mixed anhydride, which then interacts with the nucleophile:



In other words, when the reactants are introduced in this sequence, the reaction proceeds via a different, non-acid dichloride pathway and is free from the disadvantages of the latter.

It has been found that the complex of $SOCl_2$ with *N*-MP is an effective CA.[177] In this case, the reaction proceeds via a mechanism involving the formation of a Vilsmeier adduct:



Various arenesulphonyl chlorides (Table 7), used in 1982–1983[178–180] for the direct polycondensation of aromatic dicarboxylic acids with bisphenols, proved to be excellent CA. It has been established that, in the presence of pyridine alone, arenetosylates, leading to chain termination, are formed as side products together with the ester. This undesirable process was suppressed by adding to the reaction system dimethylformamide[180] as well as other amides—diethylformamide, dimethylacetamide, and *N*-MP[181]—forming Vilsmeier adducts ($R_2\overset{+}{N}$ = $CR'-O-SO_2ArCl^-$) with arenesulphonyl chloride in the presence of pyridine. For example, the polycondensation of hydroxybenzoic acid using the tosyl chloride–dimethylformamide–pyridine system afforded polyesters with η_{ln} up to 2.52 dl g^{-1}.[180] The successes achieved can be attributed to the fact that the polycondensation in the presence of arenesulphonyl chloride proceeds with formation of electrophiles (mixed anhydrides) showing a small tendency to undergo side reactions:[178]

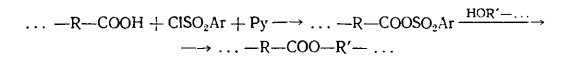
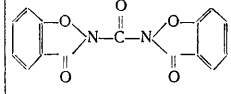
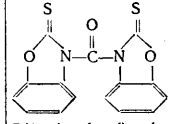
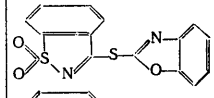
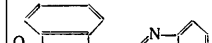
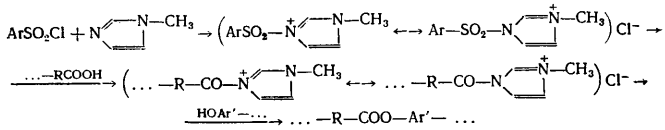


Table 7. Condensing agents (phosphorus-free) used in direct polycondensation.

No.	Condensing agent	Refs.
1	$SOCl_2$	[152, 165—177]
2	CH_3SO_2Cl	[178, 179]
3	$C_6H_5SO_2Cl$	[178, 179, 188]
4	p-$CH_3C_6H_4SO_2Cl$	[178—191]
5	2,4,6-$(CH_3)_3C_6H_2$—SO_2Cl	[178, 179, 186, 188]
6	p-Cl–$C_6H_4SO_2Cl$	[178, 179, 186, 188]
7	C_6H_5—CH_2—SO_2Cl	[186]
8	Picryl chloride	[192—194]
9	$SiCl_4$	[196—198]
10	$TiCl_4$	[199]
11		[200]
12		[201]
13	Di(p-nitrophenyl) carbonate	[202, 203]
14	Bis(2,4-dinitrophenyl) carbonate	[202, 203]
15		
16		[204, 205]
17	Dicyclohexylcarbodiimide	[206]
18	2-Chloro-1-methylpyridinium iodide	[209]
19	Chymotrypsin	[217, 218]
20	Lipase	[220]

It has been shown[182] that *N*-methylimidazole is an effective base in the polycondensation reactions indicated. The authors suggest that the reaction proceeds via the following mechanism in its presence:

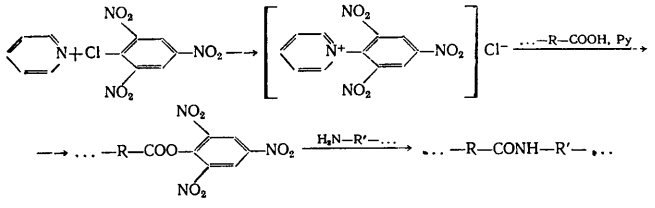


Subsequent studies[183] established that the formation of arenetosylates in the presence of pyridine can also be suppressed by the gradual introduction of phenol into a solution of the acid and tosyl chloride in pyridine. The rate at which the reagent is added has a corresponding significant influence on the molecular weight of the polyester synthesised. For example, when the duration of the addition of bisphenol A to the solution of isophthalic acid and tosyl chloride in pyridine at 120 °C is increased (from 20 to 60 min), the molecular weight of the polymer increases from 14 000 to 54 000.

A different version of polycondensation in the presence of tosyl chloride, also leading to the synthesis of high-molecular-weight polyesters, has been proposed. According to this procedure, a solution of tosyl chloride in pyridine is gradually added to a solution of the dicarboxylic acid and a bisphenol in a mixture of pyridine and dimethylformamide preheated to 120 °C over a period of 5 min.[184]

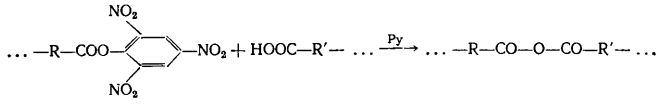
Arenesulphonyl chlorides have been used successfully to synthesise polyamides, polyesters, and polyamidoesters[185–187] and also polyesterimides.[188–191]

Picryl chloride has been used as the CA for the synthesis of polyamides[192,193] and polyesters.[192] The polymers obtained had comparatively low viscosity characteristics (η_{int} = 0.04–0.55 dl g^{-1}), although in a number of instances the viscosity of the polyamides could be raised to 0.87 dl g^{-1}.[193] On the basis of the data obtained in the study of a model reaction, the authors suggest that the reactions proceed with formation of an intermediate activated ester:

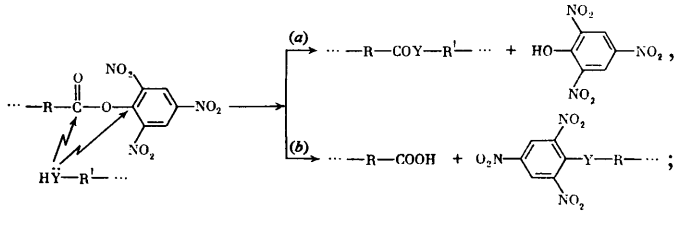


This mechanism is supported by the fact that the reaction does not occur when pyridine is replaced by triethylamine.

The formation of the carboxylic acid anhydride, in all probability as a result of the interaction of the intermediate ester with the carboxy-group, has also been observed in this process:[194]



However, the reaction could hardly be the case of the chain termination because, instead of one reactive group (activated ester group), another no less reactive (anhydride) group is produced. The aromatic nucleophilic substitution reaction (*b*), leading to the formation of relatively inactive trinitrophenyl derivatives and competing with the main reaction (*a*), constitutes a greater danger from this point of view:

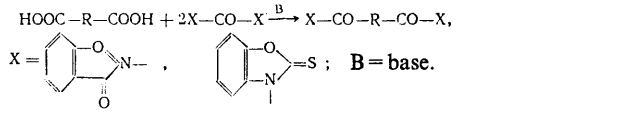


Y = O, NH.

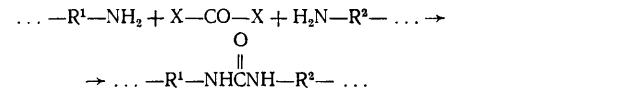
Such a reaction has been observed, for example, in the synthesis of polyamides by the polycondensation of activated nitrophenyl dicarboxylate esters with diamines, its probability increasing sharply with increase in the number of nitro-groups in the phenolic part of the ester.[195] Chain termination as a result of the formation of the trinitrophenyl derivative is also possible as a result of the interaction of the nucleophiles directly with picryl chloride or its pyridinium salt.

$SiCl_4$ proved to be an effective CA in the direct synthesis of aromatic polyamides.[196–198] Poly-*p*-benzamide with η_{ln} up to 1.97 dl g^{-1} has been obtained in its presence. $TiCl_4$ can also be used as the CA for the synthesis of polybenzamides (η_{ln} up to 0.14 dl g^{-1}).[199] The formation of SiO_2 and TiO_2 accompanies these reactions, which leads to interesting prospects for the "direct" synthesis of filled materials.

Varoius activated derivatives of carbonic acid and benzazoles (Nos. 10 and 11 in Table 7) have been used as CA in the synthesis of polyamides.[200,201] This resulted in the formation of polyamides with η_{ln} up to 0.5 dl g^{-1}. The polyamides were synthesised in two stages: the dicarboxylic acid was initially treated with the above reagent in an organic solvent in order to activate it:



The diamine was then added to the solution and the polycondensation was carried out. We may note that, if the first stage of the reaction is not quantitative, the residual CA interacts with the diamine to form urea, which leads both to a heterounit structure and to a deviation from equimolar proportions of the functional groups:



This apparently accounts for the low viscosity characteristics of the polyamides obtained. The synthesis of high-molecular-weight polyureas by the reaction of the closest analogues of compounds Nos. 11 and 12 (Table 7)—bis(*p*-nitrophenyl carbonate) and bis(2,4-dinitrophenyl carbonate) (Nos. 13 and 14)—with diamines can serve as evidence supporting the above explanation.[202,203] Incidentally, these processes can also be placed in the category of "direct polycondensation" because the reaction proceeds with formation of an intermediate activated compound (an isocyanate), reacting *in situ* with the free amine.

3-(2-Benzoxazolylthio)benzoisothiazole 1,1-dioxide and 3-(2-benzothiazolylthio)benzoisothiazole 1,1-dioxide (Nos. 15 and 16 in Table 7) have been used to synthesise polyamides by a single-stage method.[204,205] However, the above compounds have no special advantages over the appreciably more readily available CA listed above and in addition lead to the synthesis of low-molecular-weight polymers ($\eta_{int} \leqslant 0.3$ dl g^{-1} for the polyisophthalamides synthesised).

CA have been used successfully to obtain a wide variety of polymers with functional groups. For example, the synthesis of activated polyesters by treating chloro- and nitro-substituted hydroxyacids with dicyclohexylcarbodiimide in dimethylformamide has been described.[206] The polyesters obtained were used for a wide variety of purposes in peptide synthesis.[206–208] Polyesters and polyamides, suitable as polyazoradical initiators in the polymerisation of vinyl monomers, in particular, for the synthesis of block copolymers, have been synthesised by the polycondensation of azobiscyanopentanoic acid with diols and diamines using 2-chloro-2-methylpyridinium iodide as the CA.[209]

The applications of CA in polycondensation are not restricted to processes involving the direct synthesis of polymers. A wide variety of CA—dicyclohexylcarbodiimide,[210,211] $SOCl_2$,[212] trifluoroacetic acid anhydride,[211,212] triaryl phosphites,[211] and diaryl carbonates[211]—have been used successfully to obtain activated dicarboxylic acid diesters. The condensing agents Nos. 15 and 16 (Table 7) have also been used to synthesise *NN'*-bis(2-benzothiazolyl)benzene-1,3-dicarbothioate and 3,3'-isophthaloylbis(2,3-dihydro-2-thioxobenzoxazole)—an activated thioester and an activated amide of isophthalic acid respectively.[205] Activated diesters and diamides are promising polycondensation monomers for the synthesis of heterochain polymers of various classes—polyamides, polyhydrazides, polyesters, polybenzazoles, etc. Many of the CA listed in Tables 1 and 7 are suitable for the synthesis of the above monomers. The choice of a specific CA is determined by the problem formulated and also by its practical usefulness. We may note that this procedure is in many cases irreplaceable and makes it possible to synthesise activated diesters and the corresponding monomers from dicarboxylic acids to which the methods of the "direct" and traditional low-temperature polycondensation are inapplicable. For example, high-molecular-weight film- and fibre-forming polysuccinamides have been synthesised for the first time via activated diesters.[213] They are of interest from the practical point of view as self-annihilating polymers. Only low-molecular-weight polyamides have been obtained from succinic acid by direct polycondensation methods.[59] The use of activated diesters is more promising also for the synthesis of polyamides from highy basic aliphatic diamines.[212,213]

IV. Enzymes as condensing agents

It is known that under appropriate conditions the chemical equilibrium in reactions catalysed by enzymes can be displaced towards the desired product.[214] This applies also to enzymes of the class of hydrolases which under certain conditions, mainly in a non-aqueous organic medium, can be "compelled" to form heterobonds (amide and ester bonds) instead of cleaving (hydrolysing) them. This approach has acquired increasing importance in organic chemistry, for example, in the synthesis of esters,[215] peptides,[216] etc. Together with a high stereoselectivity, the advantage of enzymes is that they are used in catalytic amounts (in contrast to the chemical CA introduced in stoichiometric amounts) and are not consumed, i.e. they are virtually "eternal" CA, provided, of course, that conditions preventing their inactivation are created.[214]

In recent years studies devoted to the use of enzymes also for the solution of purely "polymeric" problems have appeared in the literature. For example, the use of chymotrypsin for the synthesis of high-molecular-weight multiblock copolymers with oligo(ethylene oxide) and oligopeptide segments[217] and the application of enzymes to the synthesis of polyaminoacids[218] have been described. The lipase-catalysed polycondensation of hydroxyacids has been achieved.[219] A short review discussing the possibilities and the prospects for the synthesis of polymers with the aid of enzymes has been published.[220]

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Summarising the data described in the review, one may conclude that the employment of CA opens a new and extremely interesting and promising chapter in the field of polycondensation. The use of CA permits the successful solution of complex problems, which it is sometimes difficult to achieve with the aid of traditional methods of synthesis. Among the principal disadvantages of the proposed CA one should include mainly their extensive consumption and the formation of equally large amounts of fairly toxic low-molecular-weight polycondensation products which are difficult to recycle and which give rise to a series of problems, including environmental ones.

Taking into account the foregoing, those systems are promising which could be readily separated, after the completion of the process, from the reaction mixture and regenerated by an appropriate treatment or, what would be even more promising, those which could be used again without additional treatment. It may be that solutions of these problems can be achieved by creating "microreactors" in the form of CA (analogous to those employed in Refs. 30, 31, 104), for example polymeric arenesulphonyl chlorides, aryl phosphites and phosphorochloridates, etc., covalently attached to polymeric supports (soluble or insoluble). It would also be of interest to attach such reagents covalently to polymers playing the role of matrices in polycondensation. Enzymes as well as artificial enzyme-like systems immobilised on polymeric carriers or in inverted micelles (possibly covalently cross-linked for stability) can also be included among promising "microreactors". The application of the above constructions might open the way to a more universal variety of direct polycondensation, which would permit syntheses under milder conditions and independently of the nature of the monomers and would promote the practical realisation of this new and promising method of synthesis of polymers.

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